

## **Comparison of AMZIRC and GRCop-84**

Henry C. de Groh III<sup>1</sup>, David Ellis<sup>1</sup>, William Loewenthal<sup>2</sup>

<sup>1</sup>NASA Glenn Research Center; 21,000 Brookpark Rd., M.S. 105-1; Cleveland OH 44135

<sup>2</sup>Ohio Aerospace Institute; 21,000 Brookpark Road; Cleveland OH 44135

Keywords: GRCop-84, AMZIRC, Copper, compression, tension, creep, mechanical properties

### **Abstract**

The mechanical properties of two copper alloys with high thermal conductivity, GRCop-84 and AMZIRC, were compared. These are competing alloys in high temperature, high heat flux applications such as rocket nozzles. The GRCop-84 data presented was taken from previous work. The results of new tensile, creep, and compression tests on AMZIRC are presented. Tests were done on as-received hard drawn material, and on material that had been subjected to a heat treatment designed to simulate a brazing operation at 935 °C. As-received AMZIRC was found to have excellent properties at temperatures below 550 °C, with room temperature yield and ultimate tensile strengths of about 500 MPa, and ductile failures. By comparison, GRCop-84's room temperature tensile yield and ultimate strengths are about 200 and 380 MPa respectively. However, the simulated brazing heat treatment substantially decreased the mechanical properties of AMZIRC; and the strength of as-received AMZIRC dropped precipitously as test temperatures exceeded 500 °C. The properties of GRCop-84 were not significantly affected by the 935 °C heat treatment. As a result, there appear to be advantages to GRCop-84 over AMZIRC if use or processing temperatures of greater than 500 °C are expected. Tensile creep tests were done at 500 and 650 °C. At these temperatures, the creep properties of GRCop-84 were superior to AMZIRC's. At equivalent rupture life and stress, GRCop-84 was found to have a 150 °C temperature advantage over AMZIRC; for equivalent rupture life and temperature GRCop-84 was two times stronger.

### **Introduction**

GRCop-84 (Cu-8 at%Cr-4 at% Nb) is a newly-developed copper alloy with an attractive balance of high temperature strength and thermal conductivity. This is the first report in a series which will detail efforts at NASA Glenn to compare GRCop-84 to similar commercial copper alloys in a consistent manner. Data on alloys such as NARloy-Z, AMZIRC, Glidcop Al-15 low oxygen grade, Cu-Cr, and Cu-Cr-Zr can be found in the literature. However, the test conditions are rarely matching for "apples-to-apples" comparisons. The alloys being considered in this work are used in high temperature applications where high thermal conductivity, high strength, and resistance to creep and low-cycle-fatigue are required. Such applications include high performance gaskets, rocket engine combustion chambers, nozzle liners, and various Reusable Launch Vehicle (RLV) technologies [1]. Figure 1 shows a schematic of a combustion chamber wherein these copper alloys might be used, particularly in the chamber liner, which is subjected to the combustion gas temperatures on the hot side and is cooled by cryogenic hydrogen flow on the back side. The tensile, creep, low-cycle-fatigue, and compressive strength of GRCop-84 will be compared to those of existing alloys, shown in Table I. This report summarizes and compares the properties of GRCop-84 to AMZIRC (Cu-0.15Zr, also known as Zirconium Copper, UNS C15000, developed by American Metal Climax, Inc.). The other alloys will be reported on later. In an effort to determine and compare the properties these alloys would actually have during use, they were tested in the "as-received" condition and after a heat treatment designed to mimic

a characteristic brazing cycle often needed in the manufacturing process [2]. The selected brazing heat treatment cycle is presented in Table II.

GRCo-84 is a precipitation hardened alloy made using rapid solidification and powder metallurgical techniques with hot isostatic pressing or extrusion and later warm and cold rolling if desired. The solubilities of Cr and Nb are very low in Cu, and Cr and Nb have a high affinity for each other, thus nearly all of the Cr and Nb combine to form the hardening intermetallic precipitate  $\text{Cr}_2\text{Nb}$ . This leaves the matrix nearly pure Cu, and the thermal conductivity of the alloy at 72% to 82% that of pure oxygen-free Cu [3]. AMZIRC however, can be cast as well as produced using powder metallurgy. Peak strengths in AMZIRC are achieved through cold work strain hardening combined with precipitation hardening and are lost if the hardened material is exposed to a high temperature braze cycle or full anneal [4]. Others have examined the properties of AMZIRC. Horn and Lewis found, as we did, that cold-worked AMZIRC retains much of its strength up to about 500 °C without becoming brittle. They also noted that the excellent strength of heavily worked rod was not achieved in their billets and that there was an inability to obtain uniform hardening in large size billets [5]. AMZIRC low-cycle-fatigue properties have been reported by Conway et al. [6] and by Hannum et al. [7]; and property reviews which have included AMZIRC have been published [8,9].

Table I. Composition of alloys in weight percent.

Alloy	Cr	Nb	Zr	Al	O	Ag
GRCo-84	6.65	5.85				
AMZIRC (C15000)			0.15			
Glidcop Al-15 (C15715)				0.15	0.17	0.17
Cu-Cr (C18200)	0.9					
Cu-Cr-Zr (C18150)	1.0		0.1			
NARLOY-Z			0.5			3.0

Table II. Vacuum heat treatment selected to simulate a chamber liner/structural jacket braze cycle.

Stage	Action
1	Raise temperature from 25 °C to 935 °C
2	Hold at 935 °C for $22.5 \pm 2.5$ min
3	Lower temperature from 935 °C to 871 °C at 1.7 °C/min
4	Lower temperature from 871 °C to 538C at 2.8 °C/min
5	Free cool to room temperature and remove specimen from furnace

### Test Procedures

The test plan includes tensile, compressive, creep, and low-cycle fatigue properties of all the alloys, though low-cycle fatigue results will be presented elsewhere. Detailed testing procedures have been presented previously [10,11,12] and will be only briefly outlined here.

All alloys will be tested in both the “as-received” condition and after the simulated braze treatment. GRCo-84 was tested in two as-received conditions: extruded, and hot-isostatically pressed (HIPed). AMZIRC was received in 0.5 inch diameter, hard drawn rods. Table II shows the heat treatment which is meant to be characteristic of a rocket nozzle liner/jacket brazing operation. Tensile tests were

conducted at 25, 200, 500, 650, and 800 °C; tests at elevated temperatures employed flowing Ar at 2.5 l/min. A strain rate of 0.005 in/in/min ( $8.3 \times 10^{-5} \text{ sec}^{-1}$ ) was used in both tensile and compression tests. Strain was measured via an extensometer attached to the gage of the tensile samples, but compression tests relied on crosshead displacement. Creep tests were done in vacuum at 500, 650, and 800 °C. The stresses in the creep tests were varied to give lives equivalent to 100 Space Shuttle missions (15 hours); for GRCop-84, creep stresses were about 100 MPa at 500 °C, 40 MPa at 650 °C, and 20 MPa at 800 °C. Stress levels for the other alloys were typically lower to achieve near 15 hour lives and to avoid failure upon loading. Creep testing of AMZIRC started with step loading tests in which the load was held constant for five hours, then raised a set amount every five hours for a total of 20 steps, or until failure. All creep tests were performed with at least two thermocouples attached to the ends of the gage area. For these creep tests, strain was measured by monitoring load train movement.

Specimen designs used for tensile, creep, and low-cycle-fatigue are shown in Appendix Figures A1, A2, and A3. Compression specimens were cylinders 5.0 mm in diameter, by 10 mm long.

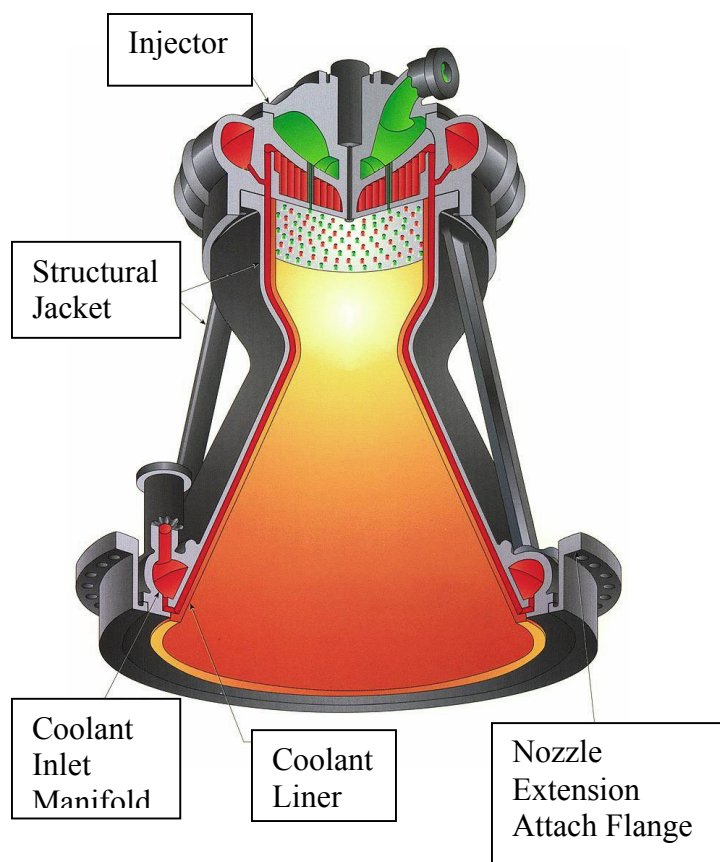


Figure 1. Schematic of regeneratively cooled combustion chamber. (borrowed from Boeing and Ref. 1)

## Test Results

### Tensile and Compression Tests

Room and elevated temperature tensile and compressive properties for AMZIRC are presented in Figures 2, 3, 4, 5 and 6, and in Table III. In Figures 2, 3, 4, and 5 data points shown for GRCop-84 are from an average of five tests; data points for AMZIRC are from the average of two tests except at the

temperatures of 400, 500, 600 and 650 °C – which were single tests (see Table III). The data shown in Figure 6 were averaged from two or three tests.

Figures 2 and 3 show as-received AMZIRC is stronger than GRCo-84 below 550 °C; but AMZIRC which has been exposed to the simulated brazing temperature of 935 °C is weaker than GRCo-84 at all temperatures. There is an abrupt drop in the strength of as-received AMZIRC near 500 °C which appears to coincide with the onset of annealing. All AMZIRC failures were ductile. Exposing AMZIRC to temperatures above 500 °C approximately tripled elongation in as-received AMZIRC (Figure 4). As the testing temperature was increased, localized necking declined, this decreased the reduction in area measurements (R/A) (Figure 5).

### **Creep Tests**

Results of step loading creep tests are shown in Figure 7 and Table IV. It can be seen in Figure 7 that at a given stress at 500 °C, the strain rate of as-received AMZIRC is about double that of GRCo-84, and the strain rate of brazed AMZIRC is about two orders of magnitude greater than GRCo-84. Similarly, strain rates of AMZIRC at 650 °C at a stress of 20 MPa are about two orders of magnitude greater than the strain rates observed for GRCo-84 at 650 °C. From our experience, a creep rate of about  $5 \times 10^{-6} \text{ sec}^{-1}$  will yield a creep rupture life of about 15 hours. At 500 °C stresses of about 60 MPa and 125 MPa applied to AMZIRC and GRCo-84 respectively are expected to yield, approximately, 15 hour lives; thus for equivalent temperatures and lives, GRCo-84 can sustain double the creep stress compared to AMZIRC. Note how close together the GRCo-84 (650 °C) and brazed AMZIRC (500 °C) curves are in Figure 7. This indicates that at equivalent stress and strain rate such as  $\sigma = 47 \text{ MPa}$  and  $\dot{\epsilon} = 10^{-6} \text{ sec}^{-1}$ , GRCo-84 can operate at temperatures 150 °C higher than AMZIRC.

Table III. AMZIRC tensile properties for as-received hard drawn material, and material given a simulated brazing cycle of 935 °C for 22 min.

Condition	Temperature (°C)	Ultimate Tensile Stress (MPa)	Yield Stress (MPa)	Elongation (%)	R/A % = 100% (Ao-Af)/Ao
As CR	25	521.2	512.9	19.0	52.8
As CR	25	500.6	491.0	20.0	61.5
As CR	200	442.8	437.5	19.9	54.6
As CR	200	445.9	439.4	18.7	54.6
As CR	400	345.2	342.9	20.1	58.6
As CR	500	265.3	262.9	21.2	62.9
As CR	600	45.3	39.8	79.3	49.2
As CR	650	33.5	28.8	82.4	52.8
As CR	800	14.3	13.3	29.8	46.6
As CR	800	15.9	14.6	99.3	51.6
Braze 935	25	232.5	33.3	47.8	77.2
Braze 935	25	233.4	32.3	43.5	74.8
Braze 935	200	177.4	28.1	46.6	72.8
Braze 935	200	184	25.8	43.0	71.4
Braze 935	400	153.2	24.5	28.9	46.4

Braze 935	500	105.9	25.2	39.8	49.8
Braze 935	600	54.2	22.7	47.5	38.8
Braze 935	650	36.1	17.2	56.7	41.9
Braze 935	800	16.8	10.8	50.0	45.4
Braze 935	800	17	9.5	39.4	31.8

$A_o$  and  $A_f$  are initial and final specimen area respectively.

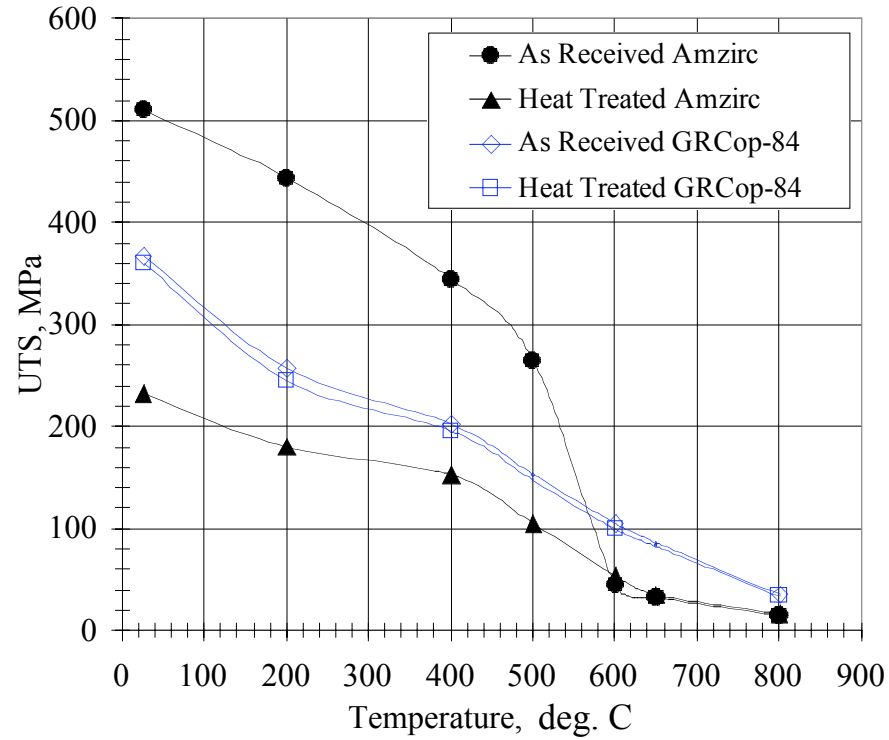


Figure 2. Ultimate tensile stress for as-received and brazed AMZIRC and GRCop-84. GRCop-84 values are the average of HIPed and extruded material.

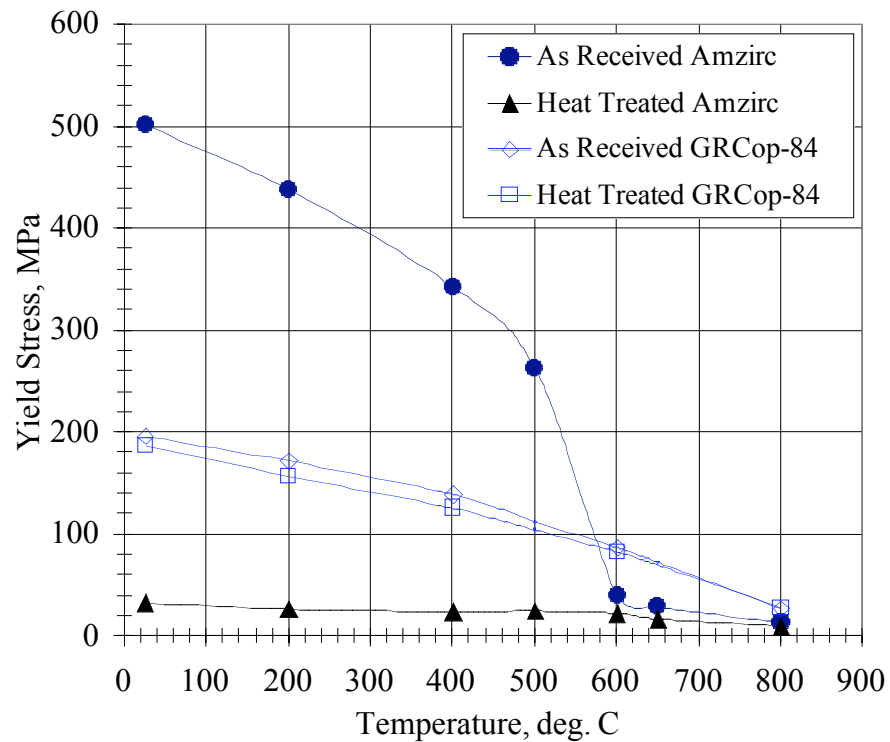


Figure 3. 0.2% offset yield strength for as-received and brazed AMZIRC and GRCop-84; GRCop-84 values are averaged HIPed and extruded material.

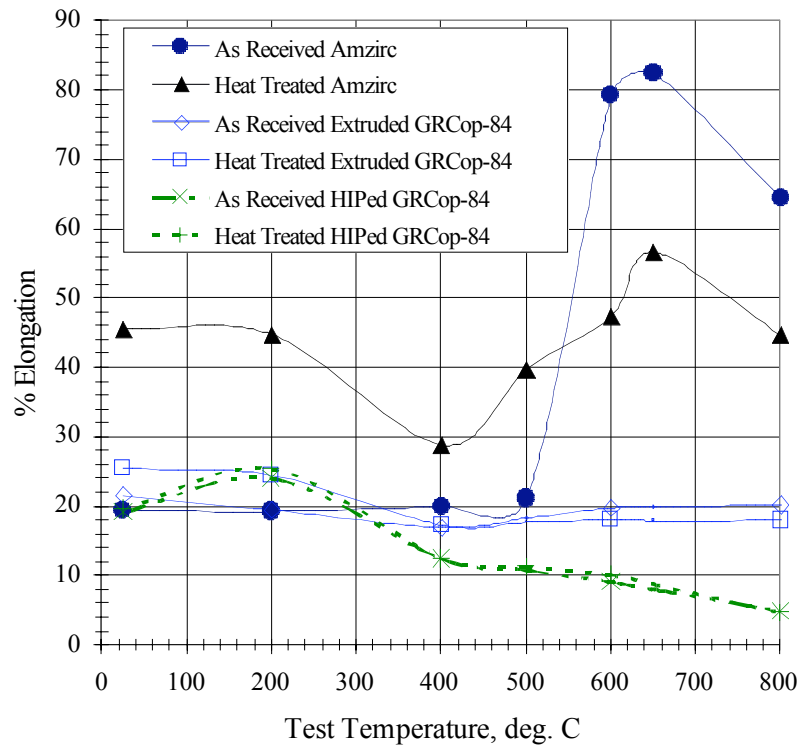


Figure 4. Tensile elongation of as-received and brazed AMZIRC and GRCop-84.

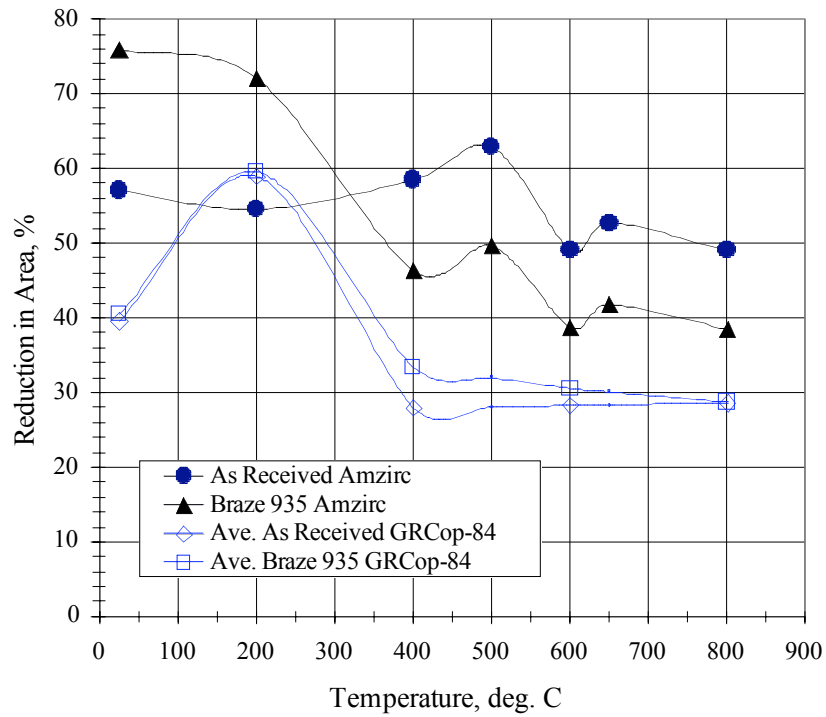


Figure 5. Reduction in cross-sectional area for as-received and brazed GRCop-84 and AMZIRC.

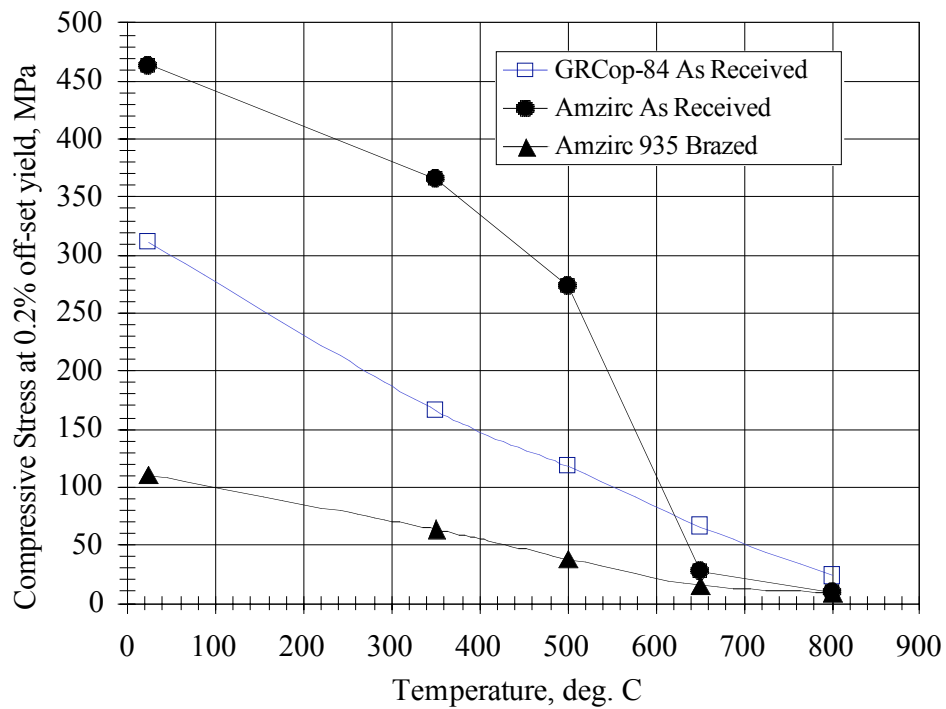


Figure 6. 0.2% offset compressive yield strength of AMZIRC and GRCop-84.

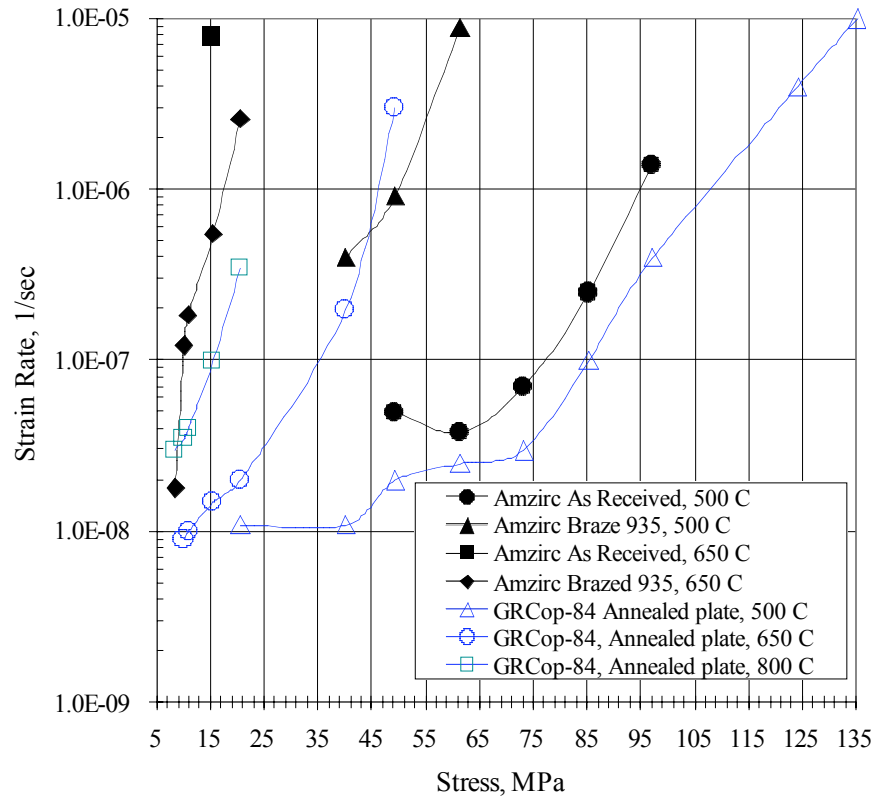


Figure 7. Strain rates at various temperatures for as-received and brazed AMZIRC and GRCop-84.

Table IV. Step loading steady-state creep rate results. Units of strain rate are  $\text{sec}^{-1}$ .

Stress, MPa	AMZIRC As Received, 500°C	AMZIRC Brazed, 500°C	AMZIRC As Received, 650°C	AMZIRC Brazed, 650°C	GRCop-84 Annealed, 500°C	GRCop-84, Annealed, 650°C	GRCop-84, Annealed, 800°C
8.35				1.80E-08			3.00E-08
9.95				1.23E-07		9.00E-09	3.50E-08
10.75				1.85E-07		1.00E-08	4.00E-08
15.40			7.80E-06	5.54E-07		1.50E-08	1.00E-07
20.40				2.60E-06	1.10E-08	2.00E-08	3.50E-07
40.00		4.03E-07			1.10E-08	2.00E-07	
49.20	5.00E-08	9.2E-07			2.00E-08	3.00E-06	
61.20	3.82E-08	9.0-06			2.50E-08		
73.10	7.00E-08				3.00E-08		
85.10	2.50E-07				1.00E-07		
97.00	1.40E-06				4.00E-07		
124.00					4.00E-06		
135.00					1.00E-05		

## Conclusions



The room and elevated temperature tensile and compressive properties of GRCop-84 and AMZIRC indicate that in the as-received, cold worked condition AMZIRC is relatively very strong and ductile. The tensile, compressive, and creep properties of AMZIRC decline rapidly as use or processing temperatures exceed 500 °C. GRCop-84 was stronger at test temperatures above 550 °C. GRCop-84 had superior creep resistance at the temperatures examined (500 and 650 °C). At equivalent stress and strain rates, GRCop-84 showed a 150 °C advantage over AMZIRC. Alternatively, at equivalent temperature and strain rates, GRCop-84 was twice as strong.

### References

- 1) Butler Jr., D.T., Pindera, M.J. "Analysis of Factors Affecting the Performance of RLV Thrust Cell Liners" NASA/CR-2004-213141, Aug. 2004.
- 2) Stephens, J.J., Schmale, D.T. "The effect of high temperature braze thermal cycles on mechanical properties of a dispersion strengthened copper alloy" SAND87-1296 UC-20, 1988 second printing.
- 3) Nathal, M.V., Ellis, D.L., Loewenthal, W.S., Raj, S.V., Thomas-Ogbuji, L.U., Ghosn, J., Greenbauer-Seng, L.A., Gayda, J., Barrett, C.A., "High conductivity materials for high heat flux applications in space propulsion systems" JANNAF 39<sup>th</sup> CS/27<sup>th</sup> APS/21<sup>st</sup> PSHS/3<sup>rd</sup> MSS Subcommittee Joint Meeting, Colorado Springs, CO, CD-ROM, (Dec. 2003), p. 2003-0390cc.
- 4) Conway, J.B., Stentz, R.H., Berling, J.T. "High temperature, low-cycle-fatigue of copper-base alloys in argon; Part I – Preliminary results for 12 alloys at 1000 °F (538 °C)" NASA CR-121259, 1973.
- 5) Horn, D.D., Lewis, H.F., "Property Investigation of Copper Base Alloys at Ambient and Elevated Temperatures" AEDC-TR-65-72, 1965, (Defense Document Center No. 467015) p. 4, 11, 12, 35, 38.
- 6) Conway, J.B., Stentz, R.H., Berling, J.T., "High-Temperature, Low-Cycle Fatigue of Copper-Base Alloys for Rocket Nozzles, Part II – Strainrange Partitioning and Low-Cycle Fatigue Results at 538 °C" NASA CR-135073, 1976.
- 7) Hannum, N.P., Kasper, H.J., Pavli, A.J., "Experimental and Theoretical Investigation of Fatigue Life in Reusable Rocket Thrust Chambers" AIAA/SAE 12<sup>th</sup> Propulsion Conf., AIAA paper No. 76-685, 1976.
- 8) Esposito, J.J., Zabora, R.F. "Thrust Chamber Life Prediction – Vol. I – Mechanical and Physical Properties of High Performance Rocket Nozzle Materials" NASA CR-134806, 1975.
- 9) Wycliffe, P.A., "Literature search on high conductivity copper based alloys" Final Report IDWA No. 6458-2, Rockwell International Sci. Center, R5739TC/sn, 1984.
- 10) Ellis, D.L., Dreshfield, R.L., "Preliminary evaluation of a powder metal copper-8 Cr-4 Nb alloy" in Advanced Earth-to-Orbit Propulsion Technology 1992, NASA CP-3174, Vol. 1., NASA MSFC, Huntsville AL, May 1992, p. 18-27.
- 11) Ellis, D.L., Dreshfield, R.L., Verrilli, M.J., Ulmer, D.G. "Mechanical Properties of a Cu-8 Cr-4 Nb alloy" in Advanced Earth-to-Orbit Propulsion Technology 1994, NASA CP-3282, NASA MSFC, Huntsville AL, May. 1994, p. 32-41.
- 12) Ellis, D.L., Michal, G.M., "Mechanical and thermal properties of two Cr-Cr-Nb alloys and NARloy-Z" NASA CR 198529, NASA Glenn Research Center, Cleveland OH, Oct. 1996.

### Appendix

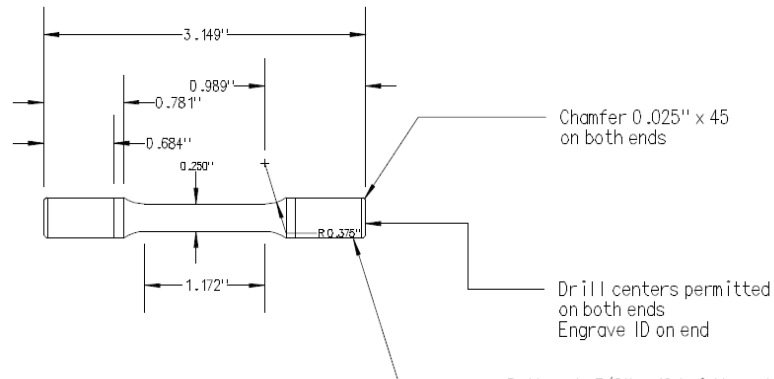


Figure A1. Specimen designed used for AMZIRC tensile and creep specimens.

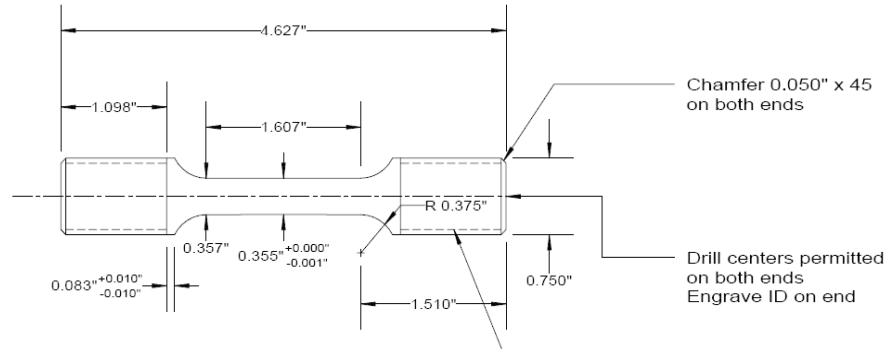


Figure A2. Tensile and creep specimen design used for GlidCop Al-15, Cu-Cr, and Cu-Cr-Zn alloys.

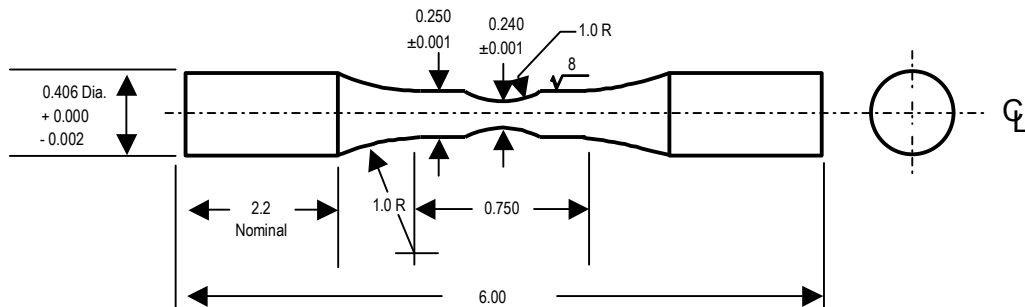


Figure A3. Low-Cycle fatigue specimen designed used for all alloys tested in LCF.